

Molecular simulation of the phase behavior of fluids and fluid mixtures using the synthetic method

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A new molecular simulation procedure is reported for determining the phase behavior of fluids and fluid mixtures, which closely follows the experimental synthetic method. The simulation procedure can be implemented using Monte Carlo or molecular dynamics in either the microcanonical or canonical statistical ensembles. Microcanonical molecular dynamics simulations are reported for the phase behavior of both the pure Lennard-Jones fluid and a Lennard-Jones mixture. The vapor pressures for the pure fluid are in good agreement with Monte Carlo Gibbs ensemble and Gibbs-Duhem calculations. The Lennard-Jones mixture is composed of equal size particles, with dissimilar energy parameters ($\epsilon_2/\epsilon_1 = 1/2$, $\epsilon_{12}/\epsilon_1 = 1/\sqrt{2}$). The binary Lennard-Jones mixture exhibits liquid-liquid equilibria at high pressures and the simulation procedure allows us to estimate the coordinates of the high-pressure branch of the critical curve. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4739853>]

I. INTRODUCTION

Understanding the phase behavior of fluids and fluid mixtures is of both considerable scientific and practical importance.¹ The phase transitions between vapor and liquid phases, different liquid phases, or solid and liquid phases are ultimately due to intermolecular interactions, which reflect both subtle and substantial differences of the molecular components of the phases involved. Differences in phase behavior have profound influences on many important industrial processes² such as enhanced oil recovery, food preparation, combustion, and transportation of fluids. In view of this it is not surprising that considerable effort is devoted both to the measurement³ and prediction of phase equilibria.⁴ In this context it should be noted that both experimental measurement and prediction have their own challenges. The measurement of phase behavior is often a labor-intensive exercise, requiring considerable skill and specialised equipment. It is also not without risks, particularly when high temperatures, pressures, and potentially toxic substances are involved. Predictions, based, for example, on equations of state,⁵ are certainly helpful but their usefulness is often restricted because of underlying theoretical limitations, which make the use of approximations unavoidable.

Molecular simulation,⁶ which provides an exact evaluation of the underlying theoretical model, is a valuable alternative to conventional calculations. In some cases,^{7,8} molecular simulation has also had a valuable role in guiding experimental work and clarifying discrepancies. Historically, the application of molecular simulation algorithms to phase equilibria was somewhat limited because of the uncertainties involved in accurately determining the chemical potential. Early attempts circumvented this problem using indirect approaches such

as thermodynamic integration⁹ and grand canonical Monte Carlo techniques.¹⁰ The Gibbs ensemble method^{11,12} represents the first direct simulation method for phase equilibria and it is now arguably the standard technique in the field. The main advantage of the Gibbs ensemble method is that the conditions for phase equilibria are achieved without the need to calculate the chemical potential. Subsequently, algorithms based on Gibbs-Duhem integration^{13,14} and histogram reweighting¹⁵ have been widely applied to pure fluids, fluid mixtures, and solid-liquid equilibria. Examples of other approaches have involved using a test particle in conjunction with an isothermal-isobaric ensemble,¹⁶ a spinodal decomposition algorithm¹⁷ to determine orthobaric densities and the combination¹⁸ of equilibrium and non-equilibrium molecular dynamics to determine solid-liquid phase equilibria.

As reviewed in Ref. 6 these alternative algorithms have well documented strengths and limitations. The Gibbs ensemble avoids the need for a physical interface but the probability of particle interchange between dense phases is low, hampering its usefulness for both high-pressure liquid-liquid and solid-liquid phase equilibria. In contrast, particle interchange is not a feature of the Gibbs-Duhem algorithm but the method is not self-starting and as such its accuracy depends on well-chosen starting conditions. Histogram reweighting provides accurate results, particularly in the vicinity of the critical point¹⁹ but it is somewhat cumbersome for multicomponent mixtures. It should also be noted that these algorithms are most easily implemented using Monte Carlo, whereas the use of molecular dynamics (MD) requires additional effort.^{18,20}

There are a variety of experimental techniques for the measurement of phase behavior, which at least partly reflects the varied conditions of interest such as high pressures and temperatures. There is not even a remote resemblance between simulation algorithms and any experimental method. This is understandable in view of the unavoidable disconnect

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between the abstract nature of theory or computation and the practical nature of experiment. In this context, the “synthetic” experimental method for high-pressure phase equilibria pioneered by Lentz and Franck^{21,22} is of particular interest because it can be mapped directly onto existing simulation techniques. The aim of this work is to exploit this correspondence to develop a simulation procedure that can be used for the high-pressure phase equilibria of mixtures. In particular, the method provides the opportunity to estimate the critical points of binary mixtures, which is difficult to achieve in a conventional simulation.

II. METHODS

A. Experimental synthetic method

First, we must briefly consider the experimental method developed by Lentz and Franck^{21,22} for high-pressure phase equilibria as it provides the rationale for the corresponding simulation procedure reported here. The method, which Lentz and Franck described as “synthetic” involves filling an autoclave of variable volume with known amounts of two components that are initially immiscible. While maintaining a constant volume, the temperature is gradually increased and the corresponding increase in pressure is monitored until the meniscus between the two phases disappears and there is only one phase. The transition represents a coexistence point on the three-dimensional pressure (p)-temperature (T)-composition (x) surface. Importantly for our purpose, a “knick point” on the pressure-temperature curve also marks the transition. Although it is impossible to observe a meniscus in a molecular simulation, a disruption in the pressure-temperature curve should be an observable simulation feature. As the pressure-temperature curve is at constant volume, it is commonly referred to as an isochore.

An example of such experimental measurements for the methane + methanol binary mixture reported in Ref. 23 is illustrated in Fig. 1. The above procedure, with composition unchanged, is subsequently repeated for several different volumes, resulting in different knick points on the various isochores. The locus of these knick points represents an isopleth at a given composition. By repeating the measurements at different compositions, different isopleths are obtained. The critical curve of the mixture can be obtained as the high temperature envelope of the isopleths. The synthetic method has been successfully used to determine the high-pressure phase behavior and critical curve of a wide variety of binary mixtures.²⁴

B. Algorithm for simulating phase equilibria

The above description suggests a simulation method that closely mirrors the experimental procedure. The constant volume autoclave at a given temperature and fixed composition is equivalent to a canonical (NVT) ensemble in which the volume (V), temperature, and the number of particles (N) are held constant. Alternatively, a microcanonical (NVE) ensemble could be used, with the fixed energy (E) being determined by the desired temperature. The simulation procedure for binary mixtures is as follows.

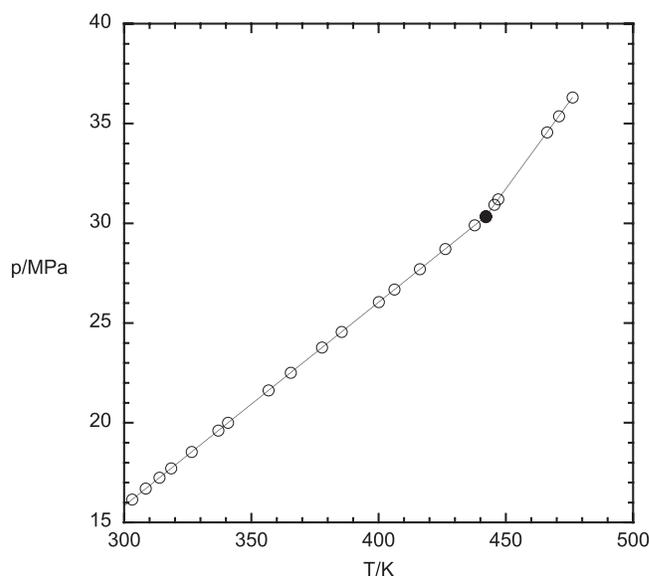


FIG. 1. An example of an experimentally determined²³ isochore (○) for a methane + methanol mixture ($x_2 = 0.451$, $V = 81.94 \text{ cm}^3 \text{ mol}^{-1}$) with a knick point (●) located at $T = 442.15 \text{ K}$ and $p = 30.35 \text{ MPa}$. An isopleth at a given constant composition is the locus of knick points obtained from different isochores. The line through the points is for guidance only.

- Determine a fixed composition ($x_2 = N_2/N$) by specifying the number of particles of component 1 (N_1) and component 2 (N_2) such that $N = N_1 + N_2$.
- For a given N and V , conduct a series of either NVE or NVT independent simulations (i) for a range of different temperatures separated by an appropriate interval ($T_{i+1} = T_i \pm \Delta T$) and monitor the pressure. The initial temperature can be either below or above the knick point temperature. An abrupt change in pressure indicates that a knick point has been passed.
- Reduce the size of ΔT and repeat (b) between the last two temperatures (T_i, T_{i-1}).
- Repeat (b) and (c) until the knick point temperature is located to within the desired level of accuracy. This provides one point on the isopleth corresponding to a particular isochore.
- To obtain additional knick points repeat (b) to (d) with different volumes but unchanged composition. The isopleth at a given composition is obtained as the locus of these knick points.

In this way the phase behavior of the mixture is obtained by simply performing repeated NVE or NVT simulations.

We monitored the change in pressure graphically but the process could in principle be automated by monitoring the derivative of pressure with respect to temperature. The procedure for calculating the temperature derivative for the NVE ensemble has been reported in Ref. 25. However, as derivatives obtain from simulations are prone to error it would be unwise to rely solely on an automated procedure without a visual inspection of the results. The main source of error is the location of the knick point temperature, which is governed by the temperature interval (ΔT). In this work, we report temperature with an uncertainty of ± 0.005 but greater accuracy could be achieved by choosing a smaller temperature interval.

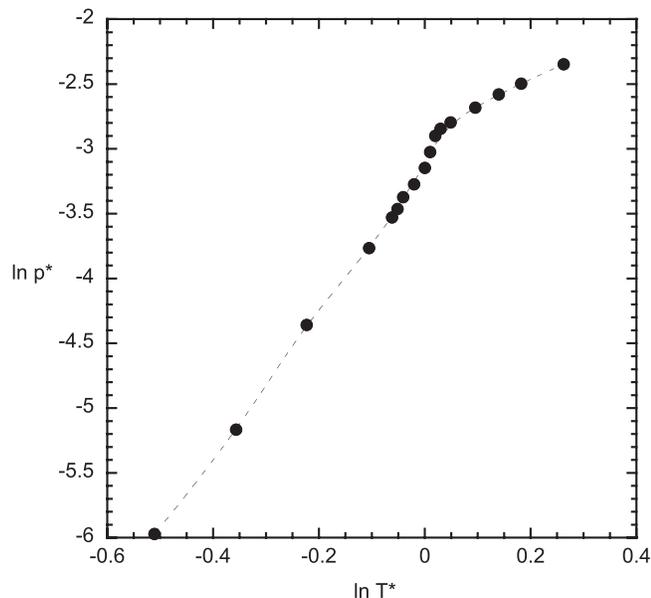


FIG. 2. An example of an isochore obtained for a binary Lennard-Jones mixture ($\rho^* = 0.1$, $x_2 = 0.1$) studied in this work. A knick point can be identified at $T^* = 1.01$, $p^* = 0.0486$. The line through the points is for guidance only.

The error in the pressure is simply the statistical uncertainty in the virial calculation for pressure at the given knick point temperature. This means that, depending on the adequacy of the simulation settings (system size, simulation length, etc.), an accurate pressure can be usually attributed to the knick point temperature.

An example of an isochore for a binary Lennard-Jones mixture is illustrated in Fig. 2, which clearly shows the knick point. Taking the logarithm of both pressure and temperature is useful in identifying the knick point. As can be observed from Fig. 2, the branches of the curve at temperatures either side of the knick point are close to linear but diverge in the proximity of the knick point. In some cases, particularly at temperatures and densities associated with a critical transition, there is considerable variability in the pressure, which makes it difficult to accurately locate the knick point. This phenomenon, which is not observed experimentally, is associated with the finite nature of the simulations. To minimize this problem a system size of at least $N = 1000$ is recommended.

The canonical ensemble is the natural ensemble for Monte Carlo simulations, whereas the microcanonical ensemble is the natural choice for molecular dynamics because Newton's equations of motion result in energy conservation. As the use of molecular dynamics for phase equilibria is relatively rare in the literature, we have opted to use it here to demonstrate the efficacy of the technique.

C. Simulation details

In this study the interaction between particles is described by the Lennard-Jones potential (u):

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (1)$$

where r is the inter-particle separation, σ and ϵ are the characteristic energy and size parameters, respectively. All the results are given in a system of reduced units, i.e., density ($\rho^* = \rho\sigma^3$), temperature ($T^* = kT/\epsilon$), pressure ($p^* = p\sigma^3/\epsilon$), and time ($\tau^* = \tau\sqrt{\epsilon/m\sigma^2}$). The asterisk superscript will be omitted in the rest of this study. The binary mixture was specified with components of equal size ($\sigma_2/\sigma_1 = 1$, $\sigma_{12}/\sigma_1 = 1$) but dissimilar energy parameters ($\epsilon_2/\epsilon_1 = 1/2$, $\epsilon_{12}/\epsilon_1 = 1/\sqrt{2}$).

A cubic simulation box was used, with the particles initially positioned on a face centred cubic (FCC) lattice. MD NVE simulations were performed by integrating the equations of motion using a five-value Gear predictor-corrector scheme⁶ with a time step of $\tau = 0.001$ and a cut-off radius of half the box length. This cut-off radius was chosen to be consistent with that used for other simulation methods such as the Gibbs ensemble¹¹ and Gibbs-Duhem¹³ methods. The results from these direct methods are typically sensitive to the cut-off value. As an alternative to using half the box length, a sufficiently large common cut-off value could be used. It has been recently reported in Ref. 26 that 6σ is sufficiently large to minimize discrepancies. We repeated some calculations with this value and the results were almost indistinguishable from those obtained with half the box length.

A desired temperature was specified at the outset of the simulation and, during the equilibration stage only, periodic velocity scaling was performed to ensure the temperature was achieved. The results for each new temperature represent a completely independent simulation, starting from a FCC lattice at a given density. The pressure was calculated via the virial theorem⁶ and the standard long-range corrections⁶ were applied to obtain the full contributions to both energy and pressure. Values of $N = 500, 1000, 2000$, and 3000 were used depending on the composition, temperature, and density. An equilibration period of $5 \times 10^5 \tau$ was typically used for equilibration, with a further period of $5 \times 10^5 \tau$ for the accumulation of ensemble averages.

III. RESULTS AND DISCUSSION

A. Vapor pressures of the pure Lennard-Jones fluid

Although binary mixtures are the main focus of this work, it occurred to us that the simulation technique could be also applied to pure components. To the best of our knowledge, the experimental synthetic method has not been applied to pure fluids, which can probably be attributed to the fact that the equipment was primarily designed for higher pressures and there are simpler methods for obtaining the vapor pressure curve. However, it is useful to apply the simulation technique to pure fluids because there are ample simulation data in the literature for comparison. The procedure for obtaining the phase coexistence of a pure fluid is the same as for the mixture, except that there is no composition variable. In this case, the isopleth curve simply becomes the vapor pressure curve.

An example of a knick point obtained for the pure Lennard-Jones fluid is given in Fig. 3. The pressure-temperature behavior of the fluid in the vicinity of the knick point reflects the nature of the fluid transition. A transition to a single liquid phase, results in either an increase (Fig. 1) or

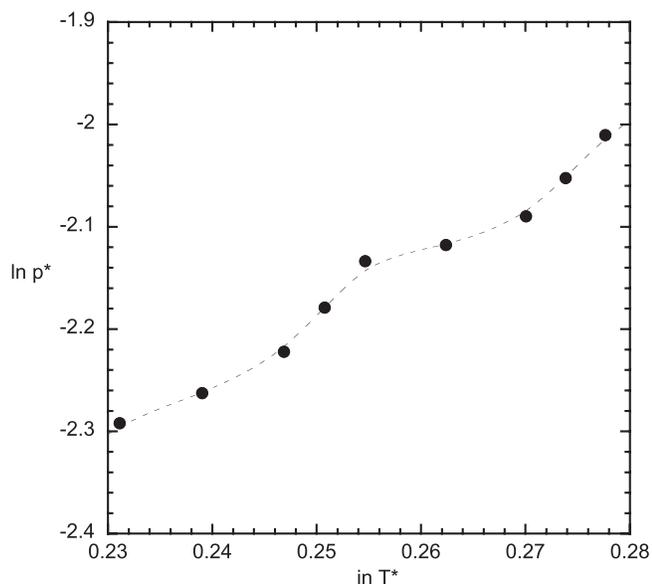


FIG. 3. An example of an isochore obtained for a pure Lennard-Jones mixture ($\rho^* = 0.295$) studied in this work. A knick point can be identified at $T^* = 1.29$, $p^* = 0.1184$. The line through the points is for guidance only.

very small decline (Fig. 6) in the pressure gradient at temperatures beyond the knick point. In contrast, a transition to a vapor phase (Figs. 2 and 3) results in a noticeably reduced pressure gradient at higher temperatures. This difference in behavior can be attributed to the difference in compressibility of vapor and liquids. The sharpness of the knick point diminishes as the coexisting phases become more similar in character. By definition, the critical point is reached when the properties of the coexisting phases become identical. $T^* = 1.29$ is close to the critical temperature of the Lennard-Jones fluid ($T^* = 1.312$) and the knick point observed at this temperature (Fig. 3) is much less sharp than is observed at lower temperatures (Fig. 2). Above the critical point, the pressure-temperature profile would be smooth and uninterrupted under all conditions because no further phase transitions are possible.

The vapor pressures of a pure Lennard-Jones fluid obtained in this work are summarized in Table I and a comparison with Monte Carlo Gibbs ensemble^{12,19,27,28} and Gibbs-Duhem²⁹ simulation data from the literature is given in Fig. 4. It is apparent from Fig. 4 that there is generally good agreement between the vapor pressures obtained here and data reported in the literature. In all cases, the discrepancies are within the combined reported uncertainties. We could not accurately resolve the vapor pressure at the critical temperature as there was a large degree of scatter at temperatures above $T^* = 1.29$. This is hardly surprising, as it is well known that finite size effects severely impede such calculations in conventional simulation techniques. It should be noted that the simulation procedure does not allow us to determine the coexisting densities of the vapor and liquid phases.

B. High-pressure phase equilibria of a binary Lennard-Jones mixture

The parameters of the binary mixture were chosen because previous work^{19,30-32} for this mixture has only reported

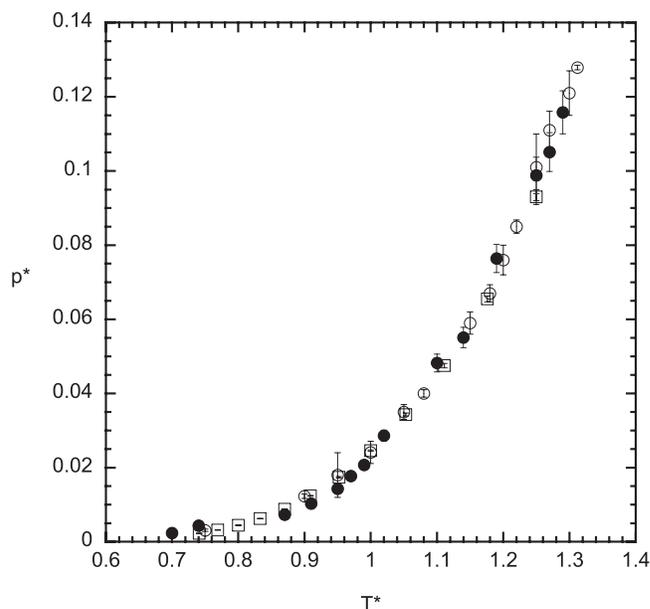


FIG. 4. Comparison of the vapor pressures of the pure Lennard-Jones fluid obtained in this work (●) with Gibbs ensemble^{12,19,27,28} (○) and Gibbs-Duhem²⁹ simulation data (□) reported elsewhere.

vapor-liquid equilibria, whereas the large difference in the energy parameters suggests that liquid-liquid equilibria at high pressure are likely. Although the synthetic simulation method also provides results for vapor-liquid equilibria, comparisons with literature calculations^{19,30-32} are not possible because the method does not yield the coexisting compositions.

The synthetic simulation procedure as described above, was used to generate different constant composition isopleths, and some of these are illustrated in Fig. 5. Examples of the knick points used to obtain the isopleths in Fig. 5 are illustrated in Fig. 6. The gentler transition through the knick point at high pressure (Fig. 6(b)) compared with lower pressure (Fig. 6(a)) reflects the greater similarity of the liquid phases in the former case.

TABLE I. Vapor pressure curve of a pure Lennard-Jones fluid obtained in this work from NVE molecular dynamics simulations.^a

T^*	p^*
0.7	0.00234(17)
0.74	0.00435(50)
0.87	0.0073(33)
0.91	0.0103(30)
0.95	0.0143(16)
0.97	0.0178(21)
0.99	0.0207(17)
1.02	0.0286(15)
1.1	0.0482(17)
1.14	0.0551(22)
1.19	0.0764(20)
1.25	0.0988(26)
1.27	0.1051(33)
1.29	0.1184(11)

^aThe values in brackets represent the standard error in last digit of the calculated pressure. The typical uncertainty in the temperatures is ± 0.005 .

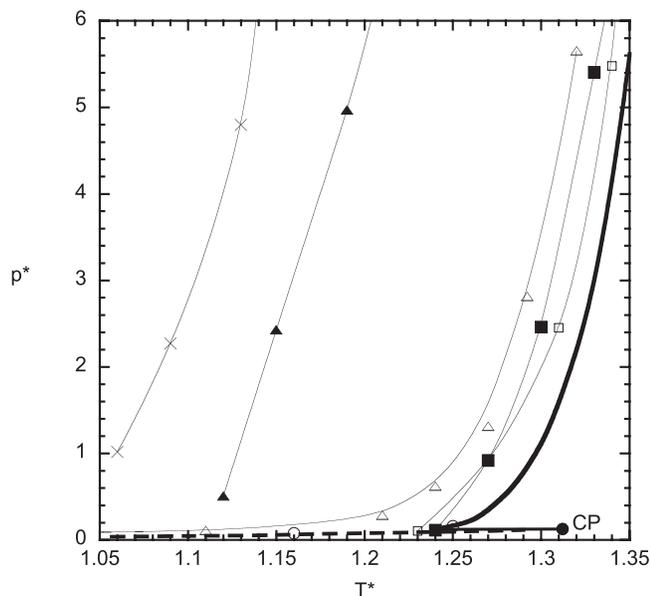


FIG. 5. Isoleths for the Lennard-Jones binary mixture at compositions of $x_2 = 0.5$ (\times), 0.4 (\blacktriangle), 0.3 (\triangle), 0.1 (\circ), 0.041 (\blacksquare), and 0.032 (\square) determined from the synthetic simulation procedure reported here. The estimated high-pressure binary mixture critical curve (—), the pure critical point (\bullet , CP) (Ref. 19) and vapor pressure curve (- - -) are also illustrated. The lines through the isopleths are for guidance only.

Two phases are observed to the left of each isopleth (Fig. 5) whereas the one phase-region occurs on the right. Therefore, the critical curve can be identified as the high temperature envelope of the isopleths. Numerical values can also be estimated by locating the pressure minimum of the liquid-liquid curves (Fig. 7) at constant temperature and these are summarized in Table II. The data in Fig. 7 were obtained by taking constant temperature slices through the isopleths.

The high-pressure critical locus for this binary mixture occurs over a very narrow range of composition. This means the critical composition at the different temperatures cannot be reliably differentiated and consequently only the critical pressures and temperatures are given in Table II. The steepness of the p - T critical curve is an obvious source of possible error in the pressure. For example, at $T^* = 1.37$, the estimated critical pressure is approximately 55 times greater than the critical pressure of the pure Lennard-Jones fluid.

Two important features of the phase behavior of the Lennard-Jones binary mixture are apparent from the shape of

TABLE II. Estimated high-pressure liquid-liquid critical curve of the binary Lennard-Jones mixture.^a

T^*	p^*
1.24	0.12
1.26	0.22
1.28	0.53
1.30	1.11
1.32	2.19
1.35	5.62
1.37	6.98

^aThe typical uncertainty in the pressures is at least ± 0.5 , particularly at high temperatures.

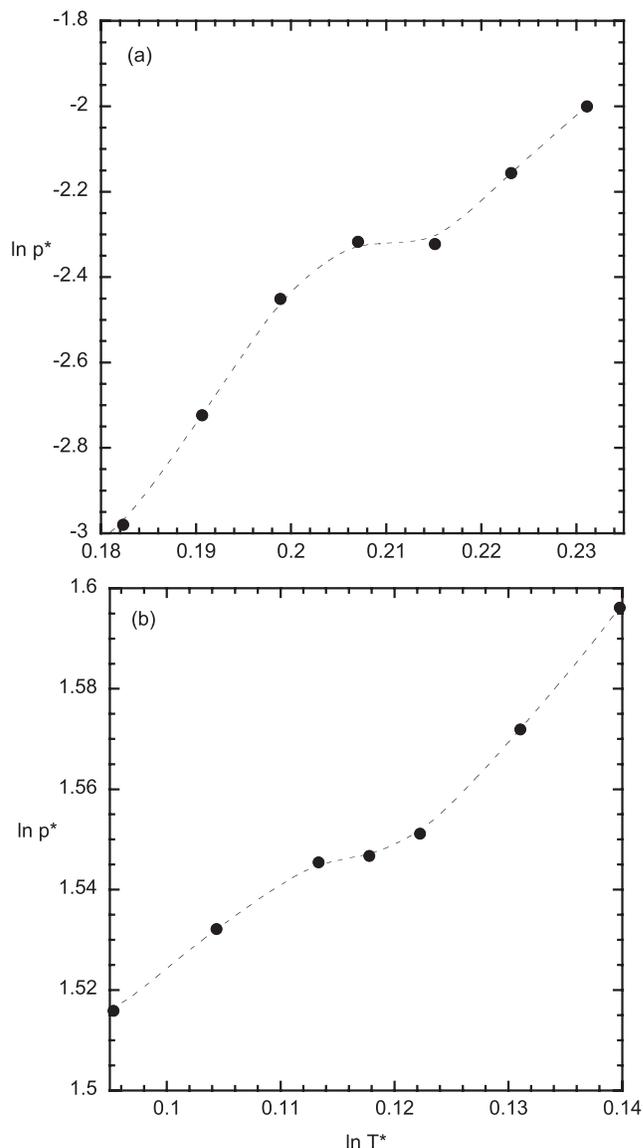


FIG. 6. Examples of isochores for the binary Lennard-Jones mixtures, showing the position of the knick points used to construct the isopleths in Fig. 5. Results are shown for (a) $x_2 = 0.032$, $\rho^* = 0.5$ (knick point at $T^* = 1.24$, $p^* = 0.098$) and (b) $x_2 = 0.5$, $\rho^* = 0.9$ (knick point at $T^* = 1.125$, $p^* = 4.696$). The lines through the points are for guidance only.

the critical curve illustrated in Fig. 5 and the location of the critical point of the pure Lennard-Jones fluid¹⁹ ($T^* = 1.312$, $p^* = 0.1279$). First, it is likely that the critical curve passes through a pressure-temperature minimum. Starting from the critical point of the pure Lennard-Jones fluid, we would expect vapor-liquid equilibria to extend partly to lower temperatures. Potoff and Panagiotopoulos reported¹⁹ a vapor-liquid critical point at $T^* = 1.0$, $p^* = 0.1522$, and $x_2 = 0.541$. In view of both the high concentration of component 2 and the relatively low temperature, this point appears to be part of the vapor-liquid branch of the critical curve commencing from the critical point of component 2 and ending at an upper critical end point of a three-phase liquid-liquid-vapor line. The high pressures ($p^* = 0.12$ – 6.98) indicate that liquid-liquid equilibria is involved and the curve passes through a pressure-temperature minimum at or near $T^* = 1.24$. Second, phase

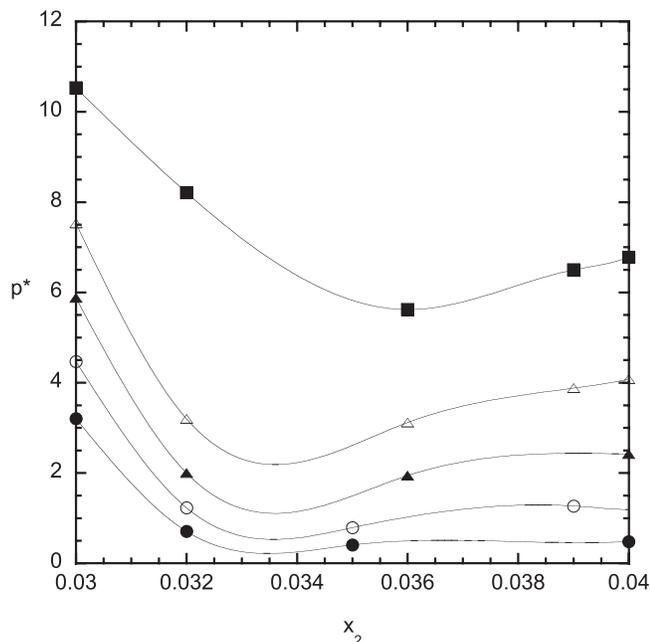


FIG. 7. Liquid-liquid equilibria at $T^* = 1.26$ (●), 1.28 (○), 1.3 (▲), 1.32 (△), and 1.35 (■) obtained from the synthetic method for the binary Lennard-Jones mixture. The lines are for guidance only.

equilibria are observed at temperatures ($T^* = 1.32$ – 1.37) that are greater than that of the critical temperature of the pure Lennard-Jones fluid. This region of fluid phase equilibria is sometimes referred to as “gas-gas immiscibility”³³ to reflect the fact that we would intuitively expect a gas at such temperatures.

In terms of the classification scheme for binary mixtures, originally proposed by van Konynenburg and Scott,³⁴ we can conclude that the Lennard-Jones binary mixture is probably a Type III system, with “gas-gas immiscibility” of the second kind.^{6,33} In contrast, Type III mixtures of the first kind of gas-gas immiscibility^{6,31} have a critical locus that extends directly to temperatures above the critical temperature of the least volatile component. Examples of real systems exhibiting Type III behavior are mixtures containing an n-alkane and either water²⁴ or a fluorocarbon^{35,36} as the other component. An alternative explanation is the mixture as a Type II system, with the critical locus representing upper critical solution temperatures, commencing from an unidentified upper critical end point at low pressures. The narrow range of compositions is consistent with Type II behavior, although the liquid-liquid critical locus of such systems typically occurs at lower temperatures.

The ability to locate liquid-liquid equilibria and hence Type III/II behavior over such a narrow range of composition is a significant advantage of the synthetic simulation procedure. The narrowness of the composition range coupled with the similar densities of the coexisting phases is likely to impose a severe impediment for conventional simulation algorithms, which rely on particle interchange between the phases. It is likely that the Gibbs ensemble method would have difficulty in distinguishing between such similar phases, resulting in the prediction of a single phase.

The synthetic simulation procedure has some other major advantages as well as some disadvantages. The main advantage is that it can be used to obtain phase equilibria using existing NVE or NVT molecular simulation programs without any additional modifications. The strategy can be implemented in both molecular dynamics and Monte Carlo, whereas applying molecular dynamics to phase equilibria with other algorithms is often difficult. In principle, a comprehensive description of the phase diagram at high pressures can be obtained and it yields an estimate of the critical curve of binary mixtures. The procedure can be easily extended to any number of components and it also closely mirrors the corresponding experimental method. Disadvantages of the method are that several state point calculations are required to identify a knick point; in some cases it is difficult to accurately identify the knick point; post-simulation analysis is required to generate the isopleths and coexistence points; and the coexisting densities are not determined.

IV. CONCLUSIONS

A new molecular simulation procedure has been developed to predict the phase behavior of both pure fluids and fluid mixtures at high pressures. The procedure can be implemented in either the microcanonical and canonical statistical ensembles using Monte Carlo or molecular dynamics techniques. A feature of the procedure is that it closely reflects the experimental synthetic method used for high-pressure phase equilibria. It can be used with existing simulation codes without the need for any modifications. Unlike alternative methods, it allows us to estimate the high-pressure critical curve of binary mixtures. Microcanonical molecular dynamics results are reported, which are in good agreement for the vapor pressures of the pure Lennard-Jones fluid. Calculations for a binary Lennard-Jones mixture indicate the existence of liquid-liquid equilibria at temperatures above both the pure critical points. This means that the mixture is either a Type III or II system. The coordinates of the high-pressure branch of the critical curve of the binary mixture are estimated.

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